Monte Carlo simulation on a system of hard cylinders at a very high packing fraction

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Using the Monte Carlo method the behavior of a system of true hard cylinders has been studied. Values of the length-to-breadth ratio L/D and packing fraction η have been chosen similar to those of real nematic liquid crystals. Results include radial distribution function $g(r)$, structure factor $S(\mathbf{k})$, and orientational order parameter M. These results lead to the conclusion that the hard cylinder model may be a useful reference for real mesomorphic phases.

It has been a long time since the discovery of the first liquid crystals at the end of nineteenth century.[1,2] Scientific interest in these mesogenic materials grew steadily until about 1930 and then began to wane. In the early 1960's renewed interest developed in liquid crystalline phases and at present there is a strong resurgence in all aspects of that research.[3] This renewed interest occurred, in part, because liquid crystals represent interesting systems in molecular physics,[4] which show a large variety of phase transitions and critical phenomena that can be thoroughly studied. The major impetus, however, is no doubt the wide range of applications in which liquid crystals have been found useful. Temperature and pressure sensing were early applications of cholesterics. However, the main interest is now centered on basic and applied research devoted to nematic applications in device engineering, mainly electro-optical components and displays.[5]

Nowadays there are three research lines that are foremost: synthesis of new mesogenic materials, research and justification of new theoretical and experimental aspects concerning the properties of liquid crystals, and, finally, the study and design of new applications.

As it is well known, the molecular geometrical features which one finds in compounds forming thermotropic liquid crystals may be summarized as follows: The molecules must be elongated, linear, and in addition they must possess a fairly rigid core structure (aromatic rings and double bonds are common along the axis of the molecule). Therefore, in order to study these systems, either by molecular-field theories or computer simulations, it is convenient to take geometrical shapes as similar to the real molecules as possible.

At present our knowledge of these systems is very limited at the molecular level. This is because of the inherent difficulties coming from developing molecular theories of dense liquids. Nevertheless, some new theories have been reported[4] in an attempt to explain the long-range orientational order observed in these phases. Computer simulation experiments have been performed by two common methods: molecular dynamics and Monte Carlo. With respect to the latter one, workers have gone from the pioneering two-dimensional runs, mainly the one reported by Vieillard-Baron,[6] with hard ellipses, to the recent three-dimensional ones, with hard ellipsoids[7] and parallel spherocylinders.[8] In spite of that, the knowledge of systems composed of nonspherical particles is very limited compared to what is known about hard-sphere systems.[9]

In particular, it would be interesting and rewarding to perform exhaustive simulations with laboratory conditions as close as possible to the real mesomorphic ones. In this connection, previous studies pointed out that great numerical difficulties would arise whenever one would try to deal with hard systems having densities and particle sizes in the range of liquid crystals.[4,10]

The aim of this work is to show that a system of true hard cylinders can actually exhibit a nematic phase for $L/D=4.44$ and $\eta=0.646$. These values have been calculated from data published for a typical nematic system *N*-(*p*-methoxybenzylidene)-*p*-butylanitine (MBBA): $L=19$ Å, $D=4.28$ Å,[11] and density [$\rho_{\text{exp}}(22\,^{\circ}\text{C})=1.049$ g/cm^{-3}].[12] In order to carry out this study we have used a canonical ensemble Monte Carlo simulation (sample size $N=150$) to obtain accurate numerical results for three quantities closely related to structural properties: pair radial distribution function $g(r)$, structure factor $S(\mathbf{k})$, and orientational order parameter M. Details of this work together with the physical interpretation of the obtained results are presented below.

The simulation box has been taken as cubic and its volume $V/D^3=809.6$ was calculated from the density ρ_{expt} and sample size N quoted above. Periodic boundary conditions have been employed in the usual way. The particular position of each cylinder, inside the simulation box, is specified by the center-of-mass position vector $\mathbf{r}_i$ and a unit vector, parallel to the cylinder long axis $\mathbf{u}_i$, which amounts to giving the polar angles θ_i and ϕ_i (Fig. 1).

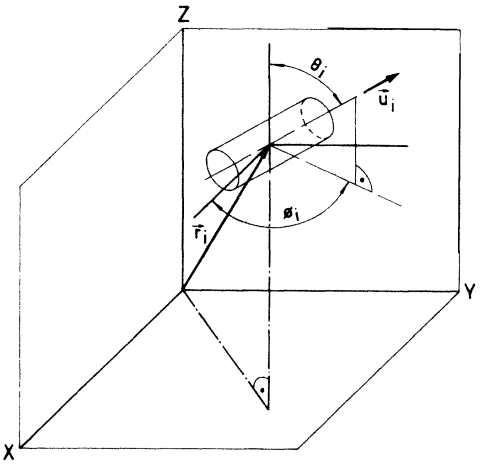

FIG. 1. The particular position of each cylinder is specified by the center-of-mass vector $\mathbf{r}_i$ and the polar angles θ_i and ϕ_i (or the vector $\mathbf{u}_i$).

The initial configuration was a simple tetragonal lattice in which cylinders are parallel to the axis Z (notice that a compact packing is not possible in our case). Markov's chain has been generated in the common way for rigid particles: (1) The cylinder to be moved is randomly chosen, (2) their vectors $\mathbf{r}_i$ and $\mathbf{u}_i$ are randomly varied, and (3) the allowed configurations are generated with use of a nonoverlapping criterion, by means of the proper geometrical conditions.

In order to evaluate the stochastic evolution of the system structure along the run and characterize the stable phase (obtained after reaching "equilibrium"), the following quantities have been computed.

(i) The pair radial distribution function $g(r)$, defined by

$$dn(r)=4\pi\rho g(r)r^2\,dr\ , \tag{1}$$

where $dn(r)$ is the number of particles around a given one, allocated between two spheres of radii r and $r+dr$, and ρ is the number density.

(ii) The structure factor $S(\mathbf{k})$,

$$S(\mathbf{k})=\frac{1}{N}\left\langle \sum_i \sum_j \cos[\mathbf{k}(\mathbf{r}_i-\mathbf{r}_j)2\pi]\right\rangle\ , \tag{2}$$

where $\mathbf{k}$ is a reciprocal-lattice proper vector, i and j vary independently from 1 to N, and angular brackets stand for the statistical average.

(iii) The orientational order parameter, M,

$$M=\frac{1}{N^2}\left\langle \sum_i \sum_j \cos(2\theta_{ij})\right\rangle,\quad \theta_{ij}=\cos^{-1}(\mathbf{u}_i\cdot\mathbf{u}_j)\ . \tag{3}$$

The values of these three quantities were computed for the initial configuration in order to check our programs. The obtained results had the foreseen values according with the expressions $S(\mathbf{k})=150$, $M=1.0$; $g(r)$ is shown in Fig. 2(b). The $g(r)$ profile and the $S(\mathbf{k})$ value indicate the existence of a spatial order like that of a crystalline solid. Moreover, the M value indicates a perfect angular orientation.

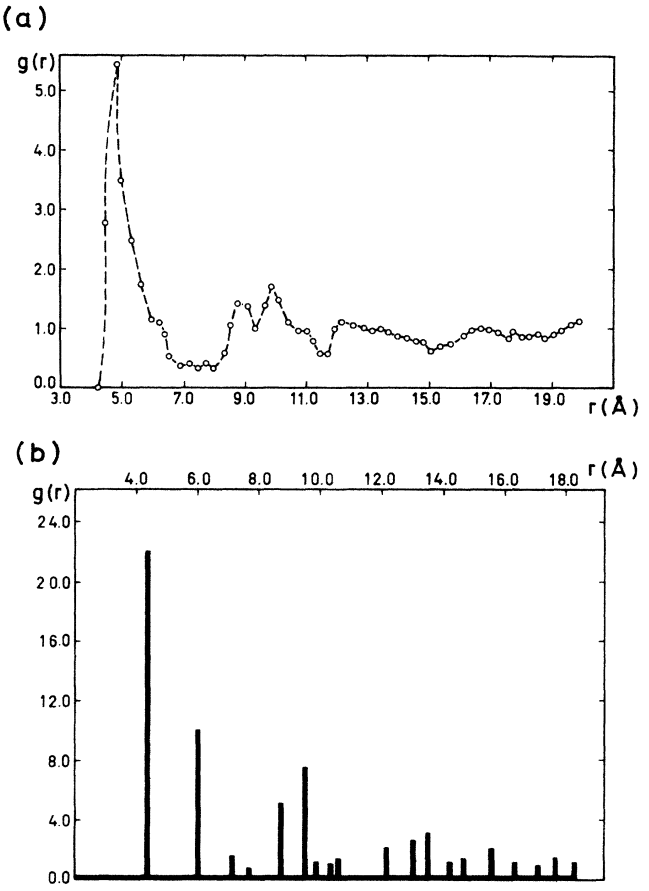

FIG. 2. The pair radial distribution function $[g(r)]$ profile: (a) nematic phase; (b) initial configuration.

The system was carried out to the "equilibrium" state. This was not a straightforward task due to two facts: first, the limited free space for sampling ($\eta=0.646$); second, the lack of an energetic criterion to decide when equilibrium is reached. With respect to the latter the usual method is to discard a large number of configurations before calculating any equilibrium property. However, in our case the quantities $S(\mathbf{k})$ and M have been computed from the very beginning to serve as indicative parameters, pointing out equilibrium closeness.

After 10^7 configurations, $S(\mathbf{k})$ indicates the loss of the

TABLE I. Stochastic evolution of the system structure along the run, where M is the orientational order parameter, $S(\mathbf{k})$ is the structure factor, and N is the number of cycles.

$10^{-6}N$	M	$S(\mathbf{k}_x)$
0.00	1.000	150.00
1.00	0.996	63.64
2.70	0.998	19.97
5.85	0.998	17.07
8.85	0.998	13.85
10.00	0.997	7.62

initial translational order shown in Fig. 2(b). Moreover, M reveals that the system is practically oriented [see $S(\mathbf{k}_x)$ and M evolutions in Table I]. Afterwards (equilibrium reached), we calculated $g(r)$, $S(\mathbf{k})$, and M by averaging over 10^4 additional configurations. The $g(r)$ profile is drawn in Fig. 2(a). On running the averaging process (acceptation rate 26%) up to 12.25×10^6 configurations, $g(r)$ and M (0.9980 ± 0.0002) remained invariant. Nevertheless, $S(\mathbf{k})$ continued to diminish until it oscillated around a typical value for isotropic distributions of center of masses [for example, $S(\mathbf{k}_x)=1.0\pm0.3$].

These results lead us to conclude that, in the studied conditions, our true hard-cylinder system exhibits a nematic phase. It is worth noting that in a recent Monte Carlo paper by Stroobants *et al.*[8] a smectic phase is predicted for L/D and η equal to ours. However, it should be stressed that (a) in that work, particles are spherocylinders, whereas in our case they are true cylinders; (b) the spherocylinders are obliged to be parallel throughout the run, and our cylinders may explore randomly all the accessible configurational space. Therefore, the higher order predicted in Ref. 8 could be a consequence of the correlations imposed by such a parallelism. In any case, it would be interesting to perform studies with our model at higher η in order to know whether or not it can exhibit smectic phases. Further details of the calculation will be the subject of a forthcoming paper.

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